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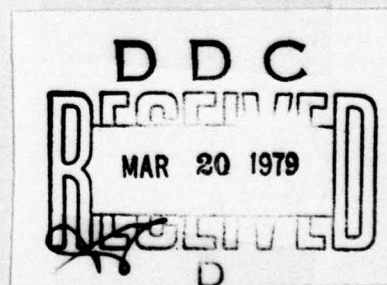
SCIENTIFIC PRINCIPLES OF TECHNOLOGY OF EXPLOSIVE-
PROOF WORK WITH INFLAMMABLE GASES AND VAPORS
(CHAPTER 7)

by

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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ё in Russian, transliterate as yё or ё.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	$sinh^{-1}$
cos	cos	ch	cosh	arc ch	$cosh^{-1}$
tg	tan	th	tanh	arc th	$tanh^{-1}$
ctg	cot	cth	coth	arc cth	$coth^{-1}$
sec	sec	sch	sech	arc sch	$sech^{-1}$
cosec	csc	csch	csch	arc csch	$csch^{-1}$

Russian	English
rot	curl
lg	log

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Chapter 7.

AVERTING THE FORMATION OF EXPLOSIVE MIXTURES OF FUEL WITH OXYGEN IN TECHNOLOGICAL PROCESSES.

1. Desensitization of explosive mixtures.

Common/general/total principles. In present chapter are examined some problems of the safeguard for explosion-proof nature of technological processes which are solved on the basis of the first the principle of safety, for the mixtures of fuel, oxygen and inert components. Such practically important methods as safeguard for tightness, the correct organization of industrial conditions/mode, which makes impossible the disturbance/breakdown of the normal motion of gas flows and so forth, from our point, are

trivial. The examination of the methods of the safeguard for explosion-proof character, which are the organization of the administration of production, does not enter in our problems.

We will be restricted (for the first principle of safety) to such processes for which special methods make it possible to make knowingly safe of the mixture of components, capable of forming explosive systems. Here are used the following methods: 1) the application/use of retarding addition; 2) the safeguard for sufficient excess of one of the components of reaction; 3) the limitation of the concentration of the missing component, oxidizer or fuel, within safe limits. To the solution of such problems, is related also the development of the methods of the dosage of dangerous component and limitation of its content in gaseous phase.

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The non-detonating mixtures, which contain fuel and oxidizer, can be divided on three categories, depending on the execution of the limitations, applied on their composition: 1) lean mixtures, $\pi < \pi_{min}$ (or $\alpha > \alpha_{max}$);   2)

rich mixtures, $\pi > \pi_{max} (\alpha < \alpha_{min})$;   3) the mixtures, retarded by inert component, $l > l_{np}$.   although the utilization of mixtures, which relate to the third category (here they are related and the mixture of explosive endothermic compounds with the inert additions), as a rule, it is the most reliable method of the safeguard for explosion-proof character, this method not always proves to be that which is applied. The dilution of the processed gases by a large quantity of inert components is usually undesirable. It retards the reactions, which are conducted during technological process, impedes the achievement of the completeness of transformation or absorption of the reacting gas, etc. Furthermore, very consumption of inert components makes the economic indices of process worse.

Is sufficiently widely used method safeguard for explosion-proof character, based on the maintenance of concentration combustible less lower concentration limit. However, this method is realized in essence only in the process of the inspection of the permissible content of combustible in the atmosphere industrial room in connection with leaks from apparatuses and gas lines. Considerably more rarely practices the limitation of the concentration of fuel in the processed mixture by the value of the lower limit

of explodability. Thus, for instance is conducted the process of the catalytic oxidation of ethylene to oxide of ethylene [173] [1].

FOOTNOTE [1]. The oxidation richer mixtures of ethylene is complicated also by the deficiency of heat withdrawal from the reaction zone, which leads to its progressive warn-up. There are indications of the possibility of overcoming this difficulty by conducting the reaction in fluidized bed [174]. ENDFOOTNOTE.

At the majority of combustible gases value π_{min} is too low, and this unavoidably will pronounce on the productivity of process. Similar conditions/mode can be justified only when value π_{min} is sufficiently great for the technological utilization of lean unburning mixtures. This, for example, occurs during the catalytic oxidation of ammonia by air for which $\pi_{min} = 15\%$ [2].

FOOTNOTE [2]. Usually are processed the mixtures, which contain 9.5-11.5o/o NH_3. ENDFOOTNOTE.

For the safeguard for explosion-proof character much more frequently is used the method of the processing/treatment of the rich mixtures of fuel and oxidizer, i.e., mixtures with $\alpha < 1$. This method open/discloses the more great possibilities of the rational administration of technological process. For its explanation and a basis, we examine in more detail the principles of retardation of explosive mixtures.

Thermal desensitization. The desensitization of burning by different additions is known long. If we are restricted to the examination of the class of the thermal stabilizers, which lower combustion temperature, then this class one should in turn, divide into two groups - inert components (CO_2, H_2O, N_2) and the addition of the complex combustible substances, which flegmatize the burning of rich mixtures.

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Inert additions retard burning, receiving the part of the thermal effect of reaction with combustion; however of these

stabilizers it occurs only an increase in the reserve of physical heat, but not chemical transformation.

More complex nature has action/effect the addition organic fuel stabilizers in the flames of rich explosive mixtures and decomposing endothermic compounds. Like purely inert additions, they do not have specific chemical effect on reaction kinetics in flame, but only they lower combustion temperature. However, such additions flegmatize burning much more active than inert components. This is caused not only (and even not so much) by their greater heat capacity which really strongly grow/increases with the complication of molecule, as by capability of these substances for endothermal transformations at high temperatures (for example, see [52]). Therefore the complex compounds, which decompose in flame, are capable of flegmatizing burning narrower in considerably smaller concentrations, than inert additions.

The obvious case of the action/effect of additions is the desensitization of the blasting decomposition of acetylene. Hydrogen, nitrogen and carbon monoxide noticeably raise the critical pressure of blasting decomposition only with the contents of the same order as as acetylene

itself. The addition of 8.4o/o butane increases critical pressure almost double [175].

The most active stabilizer of the significant part of the technological processes proves to be excess fuel itself. The utilization of excess fuel for desensitization moreover most is simple methodically and it is justified in the relation to the requirements for the technology: there is no need for for introduction into the reaction medium of alien products. So appears the popular method of the safeguard for explosion-proof character by means of processing/treatment of fuel-rich mixtures. The minimum concentration of the excess of fuel, necessary for providing for safety, can be evaluated by the standardized method taking into account the summary oxygen balance of system as a whole, i.e., taking into account the contents of all being present fuels and oxidizers.

However, in certain cases the use of excess fuel proves to be impossible or barely effective. In this case, now and then appear the facts, which make worthwhile the safeguard for explosion-proof character by the dilution of the processed mixture containing oxygen by the combustible component, which does not participate in main reaction

[176]. For this purpose most advisable are additions of hydrocarbons. Subsequently this idea is developed in more detail.

In many technological processes appears the need for an increase in permissible safe oxygen concentration, utilized as oxidizer. This will make it possible to considerably intensify the oxidation process of initial product. repeatedly it is proposed to find the possibilities of an increase in the oxygen content in the converted mixture, compensating for this approach/approximation of composition to the limits of explodability by an increase in the content of inert stabilizers.

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First of all there is in form utilization of additions of water vapor which, being condensed, easily it is removed at the subsequent stages of technological process.

The detailed investigation of regularities for the limits of the explodability of different triple and more complex mixtures (fuel - oxygen - inert component) shows that this method is largely inapplicable and the additions

of inert component ineffective. The critical value of the
excess oxidant ratio, as a rule, begins noticeably to
grow/increase only with the content of inert component in
mixture more than 40o/o. The absolute value of critical
oxygen concentration with an increase in the content of
inert component for some fuels remains invariable, more
frequent monotonically it is lowered. Subsequently this will
be illustrated in the examples of several concrete systems.

The application/use of inert diluents for the
desensitization of technological mixtures can prove to be
worthwhile only in some special cases. excess fuel it
almost always exerts the stronger quenching action/effect,
than inert component.

Decomposition of excess fuel in the rich-mixture flames
of explodability. some researchers incorrectly are considered
or must evaluate this fact. So, A. Nemeth [177], that
measured the limits of the explodability of the rich binary
mixtures of a series of hydrocarbons with oxygen and their
dependence on pressure [1], calculates the combustion
temperatures of saturated mixtures, assuming that the part
of the fuel completely reacts with all available oxygen,
and excess fuel remains invariable.

FOOTNOTE ^{1}. Let us note that all the its values r_{max} with 1 at are strongly understated. ENDFOOTNOTE.

Computed under this assumption values T_{bup} with 1 at reach at methane 3450°K, between a similar combustion temperature does not have even stoichiometric mixture $CH_4 + 2O_2$.

Application/use of inhibitors. Chemically active additions narrower in the concentrations of order 1o/o can exert the even greater quenching influence and narrow the limits of explodability, than excess fuel. This is observed, for example, with addition to the air mixtures of hydrocarbons, hydrogen, carbon monoxide, halide-containing products: CH_2ClBr, CH_3Br [178], and also CCl_4 and Cl_2 [179, 180].

The mechanism of the effect of chemically active stabilizers on burning consists in the break of the reaction chains of the basic oxidation process of fuel. Inhibitors compete with the oxidized components in reaction with the active centers of chain reaction. As a result

higher than in oconbustible, chemical affinity for the active intermediate reaction products of the oxidation of the molecule of inhibitor or products of its decomposition energetically they react with active centers, converting then into stable compounds and ceasing the development of reaction chain. Therefore the additions of inhibitor noticeably lower the concentration of active centers.

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So, haloids and aloid derivative actively react with atomic hydrogen, as which takes part in the majority of chain oxidation processes.

However, application/use chemically active addition can have only the limited interest for the safeguard for explosion-proof character in the chemical technology. cannot be used then for the solution of basic interesting ur problem - the transformation of the processed in technological processes mixtures into unburning. it is obvious that the high chemical activity of such substances will make impossible their introduction into the reacting medium during normal mode, not to mention their high cost/value.

Therefore the basic application/use of chemically active stabilizers is limited to their utilization in safety devices. In the emergency cases these products rapidly are introduced in large quantities into combustion zone or in the dangerously explosive medium which in this case fast enough is converted into unburning. Such utilization different haloid derivative in fire-extinguishinging compositions [181-183].

The specific action/effect of those inhibiting addition is limited. are most effective the derivatives of saturated hydrocarbons whose large part of the atoms of hydrogen is substituted by the atoms of haloids. Haloid derivative of organic compounds, capable of being oxidized, impede burning and decrease the normal rate of flame, apparently, only for mixtures with the excess of fuel. The addition of such products to lean mixtures can increase tribe's rate as a result of an increase in this case in the calorific value of mixture [184, 185].

Bromo derivatives are the much more active inhibitors of burning, than chlorine derivatives ones [184]. Apparently,

this is caused by the fact that the molecule of hydrogen chloride is very strong/durable and little capable of dissociation in flame. After its formation chlorine atom goes out the sphere of reaction as inhibitor, hydrogen chloride is inert product. Unlike it, hydrogen bromide easily dissociates and reacts with oxygen. Regenerated atomic bromine can again enter into reaction with atomic hydrogen.

The products, which inhibit burning, frequently are used in the so-called method of the active supression of explosions during emergency modes. This method is used for providing for safety of reservoirs with liquid fuel, for example the fuel tanks of aircraft, storages of petroleum products and the like, when above the surface of liquid there is a pad/cushion of explosive steam-air mixture. During the emergence of the center of combustion, the corresponding sensor (usually pneumatic or photoelectric) supplies signal to the automatic, so-called suppressive device.

This device is vessel with the fire-extinguishinging substance which can rapidly be introduced in large quantities into the protected reservoir with the combustion of special knock-out chuck. The sensor signal includes the

primer of knock-out chuck. Rapid quenching of flame prevents
the dangerous pressure increase in reservoir.

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For similar fittings is given out a series of patents, are
most common the instruments of the firm "Greviner" [186]
(see also [187]).

However, investigations of S. Yu. Eglit [188]
establish/installed that quenching of flame by the method of
active suppression of explosion virtually is not bonded with
the inhibition of burning by chemically active products.
Quenching bears purely thermal character and can successfully
be produced by water or flammable liquid. The achievement
of the necessary minimum density of irrigation and rate of
the throw-out extinguishing liquid is main factors of the
successful work of "suppressive" device.

The analysis of the regularities, establish/installed for
limits of the explodability of some multicomponent mixtures,
leads to the conclusion that sometimes the desensitization
of burning one of excess components proves to be not
purely thermal. Using a standardized system, it is possible

to establish that the action/effect the addition of this component bears specific, that is inherent its special chemical action/effect on the process of burning, although the here inhibiting effect not as sharply pronounced as in haloid derivative. The account of the special feature/peculiarities of each concrete techpological process facilitates the construction of the system of the safeguard for its explosion-proof character.

2. Maximum permissible oxygen content in mixtures with fuel.

Regularities for the cape of the region of explodability [189]. The safest for the technological target/purposes mixtures of fuel, oxygen and inert component whose composition corresponds to zone, which is found more to the right of the cape of the region of explodability on Fig. 47 $(l > l_{xp})$. are characterized by one important special feature/peculiarity. Experiment shows that the oxygen content in any explosive mixture of the indicated components usually is not less than in the mixture, which corresponds to cape. Any three-component mixture of oxygen, combustible and inert component is nonexplosive with the arbitrary

relationship/ratio of the contents of two latter, if in this mixture $[O_2] < Y$, where Y - the oxygen content of the cape of explodability.

It is noted [for [135] that this limiting concentration Y, is virtually identical for the majority of combustible gases and vapors. So, if we compose combustible mixtures, using enriched by nitrogen air, then for CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14}, C_2H_6, C_4H_8, C_6H_6, $(CH_3)_2CO$ this value will be within the limits of 11.0-13.5o/o. If as addition to air serves carbon dioxide, value Y for the indicated fuels will increase to 13.4-15.6o/o abs. (i.e. by approximately 20o/o) as a result of the greater heat capacity CO_2. For the mixtures of endothermic compounds - ethylene and butadiene - value Y is lower than for the majority of fuels. An especially sharp difference is observed for hydrogen, carbon monoxide and acetylene.

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The constancy of value Y of the different carbon-containing fuel/propellants is the result of those who were examined in chapter 6, pt. 4, the special feature/peculiarities of the burning of their mixtures of

lower concentration limit. The regularities, which determine the value of oxygen concentration in saturated mixture, can be quantitatively explained and used for calculation Y of experimentally unstudied combustible gases, and also the establishment of the character of dependence of Y on pressure.

It was above noted that the lower concentration limit is not changed during the partial replacement of oxygen by nitrogen. It turns out that this regularity is observed virtually up to the compositions, which correspond to the position of the cape of the region of explodability. In this case, value Y of the mixtures, flegmatized by nitrogen, differs little from oxygen content, equivalent to a quantity fuel on lower limit. This assumption makes it possible to find computed values of Y

$$Y = \nu x_{min} \tag{7.1}$$

where ν is a stoichiometric coefficient for the reaction of the complete oxidation of this fuel by oxygen. Are compared below the calculated (Y_t) and experimental (Y_{ex}) saturated oxygen contents in the combustible mixtures:

(1) Горючее	Y_{ex}	Y_t	(1) Горючее	Y_{ex}	Y_t
CH_4 . . .	12,1	10,6	C_2H_4 . . .	11,6	9,6—10,8
C_2H_6 . . .	11,0	10,5	C_3H_6 . . .	11,2	10,5
C_3H_8 . . .	11,4	11,0	CH_3OH . . .	10,3	10,9
C_4H_{10} . . .	12,1	12,5	$(CH_3)_2CO$	13,5	12,0
C_5H_{12} . . .	12,1	12,0	C_2H_2 . . .	10,0	9,3
C_6H_{14} . . .	11,9	11,4	$(CH_2—CH)_2$	10,4	11,0
C_6H_6 . . .	11,5	10,8	CO . . .	5,6	6,2

Key: (1). Fuel.

FOOTNOTE 1. According to data [135] for Y_{ex} values are borrowed there. ENDFOOTNOTE.

Experiment confirms that the difference Y_{ex} and Y_t for all investigated fuels does not exceed 15o/o of value Y. Good accord of calculated and experimental values is retained also when value Y is much lower than usual, for example for carbon monoxide. It is obvious that the replacement of excess oxygen by inert component is not essential for reaction kinetics in lean-mixture flame up to the very cape of the region of explodability - the decisive role plays the temperature constancy of burning.

The presented consideration make it possible to calculate values of Y for the unstudied combustible gases or multicomponent mixtures according to the value of lower concentration limit, i.e., actually from thermochemical data. So, for acetylene in which π_{min} = 2.5o/o, should expect Y = 6.2o/o. The possibility of calculation Y has large practical value, since the experimental determination of saturated oxygen concentration were produced only for the limited number of combustible gases and vapors. Value Ja Y is the important characteristic of explosion-proof character for a series of technological processes.

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Let us give the examples of the calculation of parameter Y, which confirm the applicability that which was presented for the compounds of different classes. Numano and Kitagawas [190] determined for acetylene-air and acetylene-oxygen mixtures under standard conditions π_{min} = 2.3o/o which corresponds $Y_t = 5.8\% O_2$ (for mixtures $C_2H_2 + O_2 + N_2$). They is experimental established Y = 5.7o/o.

For the mixtures of vinyl chloride (C_2H_3Cl) both with air and with oxygen at standard conditions the same authors

[091] will find that $\pi_{min} = 3.6\%$. Ternary mixtures C_2H_3Cl + air + N_2 cease to explode with the minimum content of air 48.1o/o independent of the concentration of fuel. This mixture contains 10.1o/o of O_2. As it will be shown in Chapter 8, with retention halo derivative hydrocarbons in the presence of the excess of oxygen, entire chlorine is virtually completely joined into hydrogen chloride; therefore for combustion C_2H_3Cl, one should accept $v = 2.5$. Equation (7.1) gives $Y_t = 9.0\%$, which satisfactorily will agree with experiment. As in the case of other endothermic compounds, value Y for a vinyl chloride is lower than common for saturated compounds. Using equation (6.13), it is possible to confirm the correctness of determination π_{min} in work [191]. For vinyl chloride Q = 278 kcal/mole, which gives $\frac{(\pi_{min}Q = 10.0)}{}$ kcal/mole in accordance with foregoing.

Since value Y is determined by the limiting concentration of fuel in lean mixtures, it is possible to assume that and the effect of pressure on change Y will be determined by the appropriate dependence for π_{min}. Since in the mixtures containing oxygen the lower limit of explodability weakly depends on pressure, it is possible to assume that value Y only insignificantly decreases with an increase of pressure. This fact is very substantial, since

the dependence of the limits of explodability from pressure little studied, but about the effect of pressure on the position of cape there is no information generally.

Technological application/appendices. In many technological processes appears the need for the pressure transfer of volatile flammable liquids, for example with their pneumatic movement and on pressure filters. To avoid the formation of the explosive mixtures of vapors of these liquids of the safety regulation for some productions, it is necessary to execute this operation with the aid of compressed nitrogen. This need is led to the complication and rise in price of production, in particular in those widespread cases when for this process it is necessary to supply large quantities of nitrogen in cylinders from other enterprises.

The operation of pressure transfer can be considerably reduced the price, if one considers that for its safety there is no need in the application/use of pure/clean nitrogen - it is necessary only so that the oxygen content in mixture would be less than Y. This fact creates two possibilities:

1. Utilization for the pressure transfer of nitrogen,

diluted by air in such relationship/ratios, that the oxygen content in the systems, which are generated after addition to the mixture of nitrogen with air of any quantities of combustible gas, remains by smaller Y [192].

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This condition is satisfied in the majority of cases narrower during the utilization of a mixture of 50o/o air + 50o/o of N_2 (final oxygen concentration it will not exceed 10.5o/o), so that the consumption of nitrogen can be abbreviated/reduced double.

2. Utilization for pressure transfer of flammable liquids of discounted and weakest gases with high content of inert components (in basic N_2 and CO_2), that are in many productions. The possibility of their application/use is defined by the fact, as is great the oxygen content in these mixtures and is how value Y for this fuel.

The question concerning the permissible oxygen content in mixture with combustible gas was raised [193] also in connection with the fact that some acting safety regulations [194] limit permissible oxygen concentration in mixtures with

combustible gases by one percent. It is obvious that this limitation without real need complicates production.

Let us note that in this question there is no unanimity: so, rules [195] for acetylene generation allow/assume the oxygen content in blowoff nitrogen up to 3o/o. Rules [196] allow possibility to solve the problem concerning the permissible oxygen content directly for enterprises themselves.

The important problem of the safeguard for explosion-proof character appears in connection with the release of apparatuses and gas lines from their filling combustible gases. This operation frequently is fulfilled in different technological processes, for example with stops for the change of conditions/mode and for the repair of equipment. As a rule, the stages of control are the most dangerously explosive stages of technological process in view of the possibility of the formation in this case of the combustible mixtures containing oxygen.

Equipment one should blow out by inert gas. usually for this is used nitrogen. However, large quantities of nitrogen are not in any production. For the execution of

scavengings, it was proposed to use as for the operations of pressure transfer, to the weakest gaseous mixture of the inert components which unavoidably contain certain quantity of oxygen. The possibility of their use for this target/purpose is determined by value of Y for gas, which is located in the air-blast apparatus.

With common for the majority of combustible gases $Y = 11-13o/o$ (if as diluent serves nitrogen) gaseous mixtures, which contain $5-6o/o$ of O_2, are completely suitable for blowing. However, position substantially is changed with blowing of the apparatuses, filled by acetylene or hydrogen, for which $Y = 5-6o/o$. In this case the nitrogen-oxygen mixture, which contains $5o/o$ of O_2, will form with the combustible gases of the mixtures, which border in composition to explosive. During the probable deviations of oxygen content from that which was assigned, appears the danger of the formation of combustible mixtures, in particular if the temperature of the air-blast apparatuses is higher than room. In such cases appears the need for the complex and expensive operation of cleaning oxygen from weakest gases.

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Between is feasible the simple method of blowing, which makes it possible to use the unpurified weakest gases, if enterprise disposes of easily attainable natural or oxy-coal gas. For this, scavenging one should produce in two stages: first by this combustible gas, i.e., virtually by methane, which has the high value of Y. In this case, is not necessary the special thoroughness of the scavenging: a reduction in the concentration of acetylene or hydrogen in the mixture of the combustible components in all 3-4 times will increase Y to the value, close to usual. Let us note that even significant (order 10o/o) foreign matter of oxygen to methane are not led to the formation of explosive mixtures.

At the second stage methane is removed by means of blowing with a mixture of inert gases. In this case, the safety is guaranteed, since the available quantities of oxygen in this case are insufficient for the formation of explosive mixtures. This method of the release of apparatuses from combustible gases will not introduce essential complications in comparison with single-stage process.

The scavenging of apparatuses must be produced when they are filled by combustible gas, but not explosive mixture. In the latter case they present large danger, and very operation of scavenging can lead to the emergence of the igniting momentum/impulse/pulses, first of all the discharges of static electricity. In the literature are described the examples of the heavy emergencies, which occurred under similar facts [197].

The examples of the execution of the technological processes in which is used the principle of the maintenance of oxygen concentration lower than Y, are examined subsequently.

3. Explosion-proof character of the mixtures, which contain the pairs of flammable liquids.

Special feature/peculiarities of vapor-gas systems. With the possibility of the formation of the explosive mixtures of vapors of flammable liquids containing oxygen we collide

first of all in widespread technological processes of the
liquid phase oxidation by air of volatile combustible
organic liquids. Such mixtures are formed also with fuel
storage liquids in large reservoirs and their pouring and
in narrower mentioned process of pressure transfer, since in
these cases above the mirror of fuel is an air cushion.

Frequently flammable liquids prove to be in contact
with the gaseous mixtures containing oxygen under the
pressure, which considerably exceeds atmospheric, which
complicates providing safety. The formation of explosive
steam-air mixtures in the atmosphere of industrial rooms
does not have any specific differences from the analogous
case with air-gas mixtures.

End section.

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Let us examine the methods of working with volatile flammable liquids, which make it possible to avoid the formation of explosive mixtures for the extent/elongation of entire technological process. In many instances these methods can be based on the existence of the temperature limits of explodability. with invariable oxygen content, equal initial (i.e. greatest, and it means and most dangerous), the equilibrium composition of the gaseous phase will be strictly fix/recorded in the case of maintenance by the constants of temperature and total pressure.

During the appropriate conditions/mode of air supply into the reactor of liquid phase oxidation or reservoir with flammable liquid (energetic bubbling, the large surface of vaporization) the air will be saturated by the pairs of the located in reactor liquids. If in this case the supplied air does not react with liquid, the composition of the gaseous phase is determined by temperature and total pressure.

The explosion-proof character of this system it is possible to provide by temperature-control of the tank with liquid fuel. If the temperature of system, and with it and the pressure of the saturated steam of liquid will be the not less specific minimum value, the content of combustible vapor will not be omitted lower than upper limit of explodability. Thermostating of reservoir feast to the necessary temperature and the saturation of air by vapor of fuel - the necessary and sufficient condition of the safeguard for explosion-proof character without any additional limitations.

Liquid phase oxidation of hydrocarbons by air [198, 199]. In the industry of organic synthesis, is widely common the method of obtaining of poliamide and polyurethane resins, synthetic fibers (caprone, nylon, perlon) and other polymeric materials from petroleum hydrocarbons. To the number of important technological processes of this type, is related the oxidation of the liquid of cyclohexane and toluene [200, 204] by air, catalyzed by the dissolved salts of heavy metals. These processes, usually done under pressure several dozens of atmospheres, are bonded with the

danger of the formation of explosive steam-air mixtures. So
that in all extent/elongation of technological cycle the
gaseous phase remains nonexplosive, were possible the
following regulations of process.

During the liquid phase oxidation of hydrocarbons, as a
rule, are not formed other (besides initial product)
volatile components, besides water, and the gaseous phase
consists of nitrogen-oxygen mixture, vapors of unreacting
hydrocarbon and water. We take, that their concentrations
reach equilibrium (for the process of vaporization) values.

In the absence of the reaction of the oxidation when
the oxygen content in vapor-gas mixture is maximal, will be
formed the most quick burning gaseous mixture. The partial
consumption of oxygen during liquid phase reaction makes
vapor-gas mixture less dangerously explosive: is sufficient
the smaller concentration of excess fuel, in order to make
impossible flame propagation. However, the dynamics of the
consumption of oxygen it is difficult to consider.

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Conducting calculation for the initial composition of

nitrogen-oxygen mixture, we obtain known safety margin".

Gaseous mixture can contain two inert components - nitrogen and water of pairs. The content of the first is invariable, the concentration of water depends on temperature. With an increase in the temperature, increases the concentration of the quenching excess fuel and the common/general/total content of inert components because of an increase in the liquid-water content. Therefore, if is establish/installed phase equilibrium, an increase in the temperature exerts favorable action/effect on the safeguard for explosion-proof character.

For determining of the quantitative characteristics of the conditions/modes of non-detonating technological process, it is necessary to give the evaluation of the concentration limits of the explodability of the mixtures containing oxygen for cyclohexane and toluene and effect on them of pressure. On the other hand, one should determine the boundaries of possible changes in the composition of the gaseous phase in the different stages of process.

The limits of explodability for both fuels are studied insufficiently: are known (moreover not it is very accurate)

only upper and lower concentration limits of their mixtures with air at atmospheric pressure. Therefore the boundaries of the region of dangerously explosive compositions and their dependence on pressure one should determine by the method of model fuel. The available experimental data are used for the check of the validity only of this approach. As standard were selected the hexane and benzene, since the combustible properties of their mixtures ¹ were studied in more detail.

FOOTNOTE ¹. Here and subsequently for brevity are indicated only combustible components of mixture (with air, oxygen and so forth). ENDFOOTNOTE.

All data on the limits of explodability are undertaken from summary [135].

The boundaries of the region of the explodability of nitrogen-air mixtures of the indicated fuels in standardized system $(\lg \alpha_{\text{нр}} - I)$ are given in Fig. 54. In this same the figure corrected values of limits for binary mixtures with oxygen - the extreme points of curve with $I = 0$. On

graph are noted also the limits of the explodability of
the air mixtures of cyclohexane, in this case is indicated
entire range of the spread of the limiting concentrations,
communicated by different authors. This range is sufficiently
great: for rich mixtures it reaches 29o/o of π_{max}.

As can be seen from curve/graph, the standardized
characteristics of the limits of explosiveness of hexane,
benzene and cyclohexane in the which interests us region
are sufficiently close between themselves. This confirms the
possibility of propagation for cyclohexane of the dependences
of critical conditions on the content of inert component
and pressure, establish/installed for a hexane.

Further are examined two modes of the oxidation of
cyclohexane - with 18 and 35 at. The limits of the
explodability of the air mixtures of hexane are studied to
maximum pressure 12 at and T = 150°C. It is
establish/installed that with p > 4 at there are two
limits of the explodability of the rich mixtures: for hot
and cold flames.

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Us interest only the conditions of the emergence of hot flame; cold flame is here safe, since the possibility of its transition to hot flame is excluded. The extrapolated boundary of the propagation of hot flame with 150°C to 18 at. we find the unknown position of the limit of explodability, shown on the graph by cut 4.

The change in the composition of pro-gas mixture with temperature, which corresponds to that condition that oxygen is not expend/consumed on liquid phase reaction, can be determined by thermodynamic calculation. The example of such a calculation for the oxidation processes of cyclohexane at common/general/total constant pressure 18 and 35 at illustrates table 13. In it the reduced pressures that which was saturated the pair of both liquid components at the appropriate temperatures. partial air pressure, and also, therefore, the partial pressures of oxygen and nitrogen can be determined by the difference between total pressure p_0 and the sum of the partial pressures of saturated vapors of C_6H_{12} and H_2O. Hence is located the sum of the partial pressures of the inert components $N_2 + H_2O$ and corresponding values I (in o/o) and α.
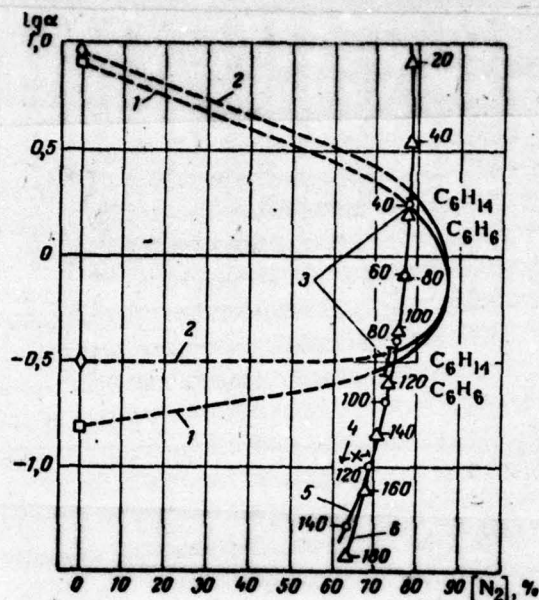
Fig. 54. Limits of explodability for nitrogen-oxygen mixtures of hexane, benzene and cyclohexane and change in composition of equilibrium vapor-gas mixture $C_6H_{12} + H_2O + O_2 + N_2$ with temperature: 1 - limits in system $C_6H_{14} + O_2 + N_2$ p = 1 of at, T = 20°C; 2 - the same, for benzene, 3 - the same, for cyclohexane; 4 - the same, for mixture C_6H_{14} + air, p = of 18 at, T = 150°C; 5 - change in equilibrium composition of mixture $C_6H_{12} + H_2O$ + air, p_0 = 18 at; 6. the same, p_0 = 35 at.

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The equilibrium compositions of the mixtures of air, vapors of cyclohexane and water on the graph of Fig. 54 for total pressure 18 and 35 at are compared with the limits of explodability in system $C_6H_{12} - O_2 - N_2$. Here o subsequently is considered the summary content of both inert components, i.e., it is accepted that water is replaced by an equivalent quantity of nitrogen. Under this assumption the actual boundaries of the region of explodability somewhat those narrower designed. For each point, which characterizes the composition of equilibrium mixture, numerals showed the corresponding to this composition temperature. the curves of equilibrium compositions for total pressure 18 and 35 at almost completely are superimposed to each other; however, the temperatures, which correspond to identical compositions, in them are substantially distinct, which is shown on graph.

With a temperature decrease of equilibrium vapor-gas mixture, the value of the excess oxidant ratio continuously increases. At specific minimum temperature in the point of intersection of curves for the limits of explosiveness and change in the equilibrium composition, the mixture becomes explosive. As shows the comparison of curves, when total pressure is equal to 18 at, this occurs at temperature of

approximately 120°C.

Equilibrium vapor-gas mixture remains explosive up to T
= 40°C, when the concentration of cyclohexane decreases to
the value, which corresponds to lower concentration limit.
The extrapolation of the available data on the limits of
explodability to 35 at - another conditions/mode of
technological process - makes it possible to give the rough
(although less accurate) estimate of saturated safe
temperature; with T > 180°C, equilibrium mixture still
remains non-detonating.

Table 13. Calculation of the equilibrium composition of vapor-gas mixture in air - cyclohexane - water system.

T, °C	(1) Давление насыщенного пара, am		(2) Парциальные давления, am				l, %		α	
			N₂+H₂O		O₂					
	C_6H_{12}	H_2O	$p_0=18$	$p_0=35$	$p_0=18$	$p_0=35$	$p_0=18$	$p_0=35$	$p_0=18$	$p_0=35$
200	13,1	15,3	—	20,5	—	1,39	—	58,6	—	0,0154
180	9,47	9,88	—	22,2	—	3,29	—	63,5	—	0,0385
160	6,62	6,10	—	23,7	—	4,68	—	67,7	—	0,0785
140	4,42	3,57	11,5	24,9	2,10	5,67	63,8	71,2	0,0528	0,143
120	2,83	1,96	12,4	25,8	2,77	6,34	69,1	73,8	0,102	0,249
100	1,72	1,00	13,1	26,5	3,21	6,78	72,6	75,7	0,208	0,439
80	0,975	0,461	13,5	27,0	3,48	7,05	75,3	77,1	0,396	0,803
60	0,507	0,197	13,9	27,3	3,63	7,20	77,2	78,0	0,794	1,58
40	0,239	0,073	14,1	27,5	3,71	7,28	78,2	78,5	1,73	3,34
20	0,101	0,023	—	27,6	—	7,32	—	78,8	—	8,06

Key: (1). Pressure of saturated steam, ats. (2). Partial pressure, at.

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The method of thermostating makes it possible to solve the question concerning the conditions of explosion-proof character for the reactor of oxidation. However, by this is not contained by the problem of providing safety of entire technological process as a whole. At its subsequent stages the reaction gases, saturated with oxidizable substance, must be cooled. In this case, begins the condensation of excess (for the process of burning) fuel whose presence made the

steam-gas system of safe.

During sufficient cooling equilibrium concentration of fuel in vapor-gas mixture becomes less π_{min}. However, this cooling does not still guarantee the equilibrium of gas and liquid phases, but it means the explosion-proof character of process. During the rapid cooling of saturated vapor which is formed the stable fog of liquid fuel, and its content in the gaseous phase remains due to this super-equilibrium. Fog-air mixtures can explode just as gas. It is establish/installed [178] that the explosiveness of lean fog-air systems does not have vital differences from the explosiveness of purely gaseous mixtures with the equal content of fuel.

Thus, the explosion-proof character of the cooled gaseous oxidation products cannot be secured by obtaining the mixtures which have $\pi < \pi_{min}$. however, problem can be solved by another method, by means of monitoring of satisfaction of condition $[O_2] < Y$. In the process of liquid phase oxidation, oxygen concentration in the gaseous phase decreases. with the sufficient degree of its spending, oxygen concentration is lowered to value, smaller Y, and mixture becomes nonexplosive, independent of the content into

nonflammable. The problem of providing safety of the gases, which emerge from reactor, is reduced to the uninterrupted monitoring of the content in them of oxygen. For this, can be used the automatic magnetic gas analyzers of oxygen of the type MGK.

As shown above, for the hydrocarbons Y in question it must be equal from 10 to 13o/o; equation (7.1) gives $Y_t =$ $= 11.7\%$ for cyclohexane $(\pi_{min} = 1,3\%)$ and $Y_t = 12,6\%$ for toluene $(\pi_{min} = 1,4\%)$. It is difficult to expect so that these values substantially will change with a pressure increase (above 1 at). Therefore the maximum permissible oxygen concentration at output/yield from reactor should establish/install equal to 7o/o for both hydrocarbons. Experiment shows that this condition is feasible during the normal flow of technological process.

If the realization of this conditions/mode for cyclohexane or another hydrocarbon proves to be for some reason or other difficult, it is expedient to dilute the fresh air, which enters in the rector of oxidation, by the emerging from it gases, i.e., to produce partial recirculation. Apparently, this noticeably does not hamper the course of liquid phase reaction, in any case, for the

oxidation of cyclohexane, since the rate of this process barely depends on oxygen content [200, 201].

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It is experimentally establish/installed that during the oxidation of toluene (unlike cyclohexane) there is no liquid water in reactor. Therefore during the calculation of the equilibrium composition of vapor-gas mixture, is used $[H_2O]$ = 0. The nonregulated additions of unsaturated water vapor to toluene-air mixture are not considered that their presence increases "safety margin". A change in the composition of equilibrium Toluene-air mixtures with the invariable oxygen content for p_0 = 2 at and p_0 = 20 at is shown in Fig. 55.

On the same graph are given boundaries of the region established/installed earlier of explodability with 1 at, and also values of limits for the air mixtures of toluene. Processing of available data on the effect of pressure on the limits of the explodability of the mixtures of hexane makes it possible to approximately evaluate the angular coefficient

$$-\frac{d\lg a_{min}}{d\lg p} = 0.35 \qquad (7.2)$$

However, these data correspond to nonisothermal conditions/mode.
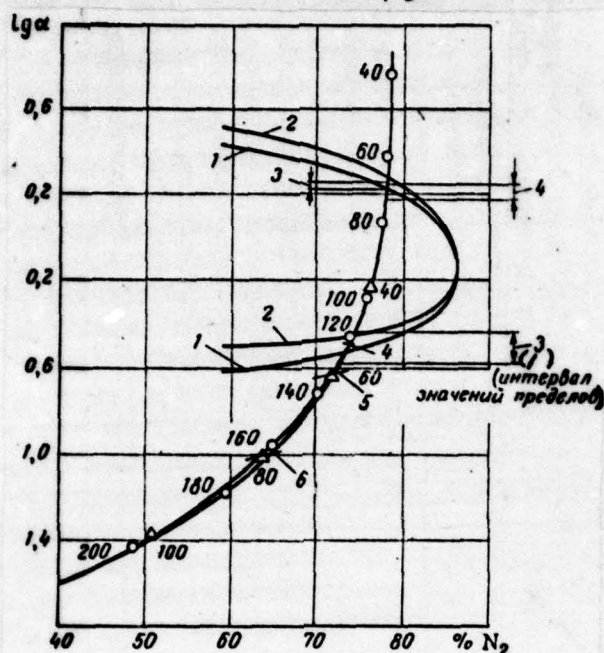
Fig. 55. Limits of explodability of mixtures of hydrocarbons and change in composition of equilibrium mixture $C_7H_8 + H_2O + O_2 + N_2$: 1 - limits of explodability with 1 at for hexane; 2 - the same, for benzene; 3 - the same, for cyclohexane; 4 - the same, for toluene; 5 - limit of explodability with 2 at; 6 - the same, with 20 at; Δ - equilibrium composition with 2 at; ϴ - the same, with 20 at.

Key: (1). an interval of values of limits.

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Accepting in accordance with that which was presented in chapter 6, section. 2, that value π_{max} grow/increases by 14o/o with an increase in the temperature by 100 degrees, it is possible to introduce interference correction of temperature and to calculate the isothermal baric coefficient of the critical conditions

$$-\left(\frac{\partial \lg \alpha_{min}}{\partial \lg p}\right)_{T-const} = 0.29 \qquad (7.2a)$$

Using values of the baric and temperature coefficients of the limits of explodability, it is possible to calculate the positions of the limits of explodability for the assigned initial pressures which are shown in Fig. 55.

Determining the points of intersection of the corresponding curves for equilibrium compositions and the limits of explodability and interpolating values of critical temperature, we find the dependence of the latter on total pressure. So, with 2 at curves intersect at point lg α = -0.64; I = 72o/o (N_2), equilibrium steam-gas mixture has this composition at temperature of approximately 60°C. Fig. 56 illustrates a change in the saturated modes of the non-detonating liquid phase oxidation of toluene by air with

an increase of pressure.

For the creation of the specific "safety margin" the temperature of liquid in the reactor of oxidation must be by 20-30 degrees higher than critical, determined by the graph of Fig. 56. It is possible to expect that refinement of the data on the limits of explodability in toluene-oxygen - nitrogen system during the most thorough investigation will not give the bases to change presented in Fig. 56 values of critical temperature more than for 15 degrees, but saturated oxygen concentration - are more than to 2o/o abs.

In work [205] is studied the effect of pressure on the limits of the explodability of toluene-air mixtures; however, the results of these experiments were uncertain. That which was found here for η at $\pi_{max} = 7,2\%$ virtually coincides with the data of earlier determinations. However, for large pressures with 180°C in two sets of experiments on incomprehensible reason, are obtained two series of values π_{max}, whose difference reaches 40o/o of measured value. To both series they correspond the approximate values $d\lg\alpha_{max}/d\lg p = 0,35$ and 0.50, last/latter number is also doubtful. In other results of this work, the disagreement of those who

were measured π_{max} reaches 100o/o.

It is obvious that the data of this study are partially erroneous, which is caused by the complexity of experimentation with vapor-gas mixtures. The results of work obviously illustrate worthwhileness of application/use and advantage of the method of modelling for such systems.
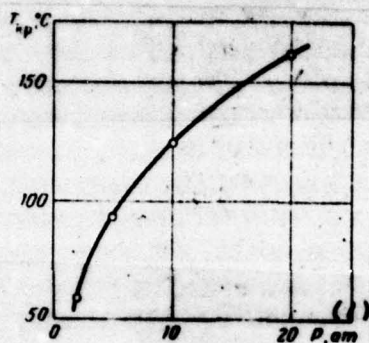
Fig. 56. Saturated modes of non-detonating liquid phase oxidation of toluene by air.

Key: (1). at.

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Are more reliable the obtained in this work characteristics of the cape of the region of explodability. In 1 at and 180°C, it corresponds 87o/o of N_2 and 11.4o/o of O_2. Assuming that the temperature correction for Y is 8o/o to 100 degrees, as for π_{min}, we find for room temperature of Y = 13.0o/o in accordance with the made above estimation.

The air cushion above the surface of flammable liquid [206, 207]. Some highly volatile flammable liquids under

specific conditions can be stored in reservoirs and crushed by directly atmospheric air without dilution by nitrogen. These conditions become possible as a result of high pressure the pair of flammable liquid, sufficient for the formation of nonexplosive mixtures with the content of fuel, that exceed x_{max} is narrower at the temperatures of close to room.

This method can be applied in warm season either in hot climate or in the heated compartments. It is especially advisable when compressed nitrogen generally proves to be unattainable, for example with bottling from cisterns on the unsteady pads.

For the realization of this method it is necessary for the extent/elongation entire operation to track the temperature of liquid in reservoir. It must not be lower than certain limiting value, the greater, than higher total pressure above the surface of liquid. The air, supplied into reservoir, must be saturated by vapor of fuel. For this, it it is expedient to let pass through the filling column, filled by Raschig rings, irrigated by liquid from reservoir. The temperature of column is maintained somewhat the greater temperature basic reservoir, which guarantees the

completeness of saturation [1].

FOOTNOTE [1]. Let us give the example of the utilization of a column for saturation.

Is used column by height 125 cm and by diameter 12 cm, filled by packing from Raschig rings by size/dimension 15 x 15 x 2 mm with the consumption of air 60 m^3/h (volume derived for standard conditions) and the irrigating liquid 100 l/h; with p = 2, at linear air-stream velocity in the clear opening of column is equal to 0.7 m/s. In this case the degree of saturation by vapor of the air, passed through the column, reaches 90o/o. ENDFOOTNOTE.

The saturated safe temperature of pressure transfer by air $T_{кр}$ is determined by the factors, specific for this liquid: by the value π_{max} of air mixtures and by the pressure of the saturated steam.

Are given below the minimum safe temperatures $T_{КР}(°C)$ for a pressure transfer by air of benzene of acetone, of ethyl ether and ethyl mixture P - 9 [2] at total pressure

1 and 2 at.

FOOTNOTE 2. It is used as antiknock components to motor
fuels, its basic volatile component is ethyl bromide.
ENDFOOTNOTE.

	(1) 1 am	2 am
C_2H_6	19	33
$(CH_3)_2CO$	8	22
$(C_2H_5)_2O$	15	32
$P - 9$	2	18

Key: (1). at.

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Hence it follows that value $T_{кp}$ sufficiently moderate
for, this method could be suitable to practical utilization.
For providing "safety margin" the temperature of the crushed
liquid must be maintained to 5-6°C greater $T_{кp}$

4. Mixtures with the noncondensing fuel.

Gas-phase conversion of hydrocarbons at the temperatures, close to T_i [208, 209]. In technology of organic synthesis, are known the processes of the gas-phase partial oxidation of hydrocarbons by pure/clean oxygen for the target/purpose of obtaining alcohols, aldehydes, ketones and carboxylic acids. These processes are conducted usually at 300-500°C, i.e., at the temperatures, commensurable with spontaneous ignition temperatures. Here are converted the nonexplosive mixtures, fuel-rich.

For the safeguard for explosion-proof character of technological process, they limit the permissible oxygen content in the processed mixtures. At the same time for the intensification of process, is desirable a possible increase in oxygen concentration. Since in this case fuel in gaseous mixture is not located in equilibrium with its liquid phase, the explosion-proof character of process is no longer reached by thermal control. However, for a gas-phase system it is possible to arbitrarily maintain the non-detonating composition of mixture.

It was establish/installed that for fractions C_3-C_4 with 1 at critical oxygen concentration is 46-52o/o. The conversion of hydrocarbon-oxygen mixtures is possible safely

to conduct with proper safety margin with oxygen
concentration to 35-38o/o.

Table 14 gives the results of determining the limits
of explodability under standard conditions for the mixtures
of technical hydrocarbons with oxygen, some mixtures contain
also carbon monoxide. Indicating compositions, we will
designate by (C_4H_{10}) - technical butane, which contains
94o/o of basic product; by (C_3H_6) - technical propylene,
which contains 89o/o of pure/clean propylene, 6o/o of
propane; by (C_3H_6) - propane-propylene fraction which are
45o/o of propane, 30o/o of propylene, 16o/o of ethane.
Values $\alpha_{кр}$ are calculated taking into account the actual
composition of complex fuel.

Comparison shows that standardized values of the
critical conditions of the explodability of the complex
mixtures of hydrocarbons in principle do not differ from
the same for individual saturated hydrocarbons and propylene
(according to data [135]:

(1)Углеводород	C_3H_8	C_3H_6	C_4H_{10}	C_2H_6
α_{min}	0,147	0,164	0,160	0,197

Key: (1). Hydrocarbon.

The moist mixtures of carbon monoxide are combustible in the even more broad band of the compositions: for binary mixture CO + O_2 under standard conditions $\alpha_{min} = 0.13$. It was necessary to consider effect the addition of carbon monoxide on the limits of explodability, since it is formed as by-product during the oxidation of hydrocarbons.

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It turned out that the additions of carbon monoxide to hydrocarbons not only do not expand the region of explodability for hydrocarbons [1], but they flegmatize these mixtures, giving sometimes to increase critical concentration of oxygen to 63 o/o and α_{min} to 0.75.

FOOTNOTE [1]. In spite of the smaller effective heat capacity of carbon monoxide, incapable of endothermal reactions in flame. ENDFOOTNOTE.

Thus, upper concentration limit is lowered to the composition, close to stoichiometric. Value α_{min} grow/increases almost double with addition to fuel 15-20 o/o of carbon

monoxide, and during dilution by it double - to 4.5 times.

The narrowing of the region of combustible compositions during the partial replacement in the rich mixtures of hydrocarbon by carbon monoxide testifies to distinctly expressed mutual inhibition of their oxidation. This replacement of components is bonded with an increase in temperature of burning; however, for flame propagation, occur less favorable conditions.

Figures 57 depicts the results of the investigation of critical values of the excess oxidant ratio for the mixtures of technical propylene with oxygen (83o/o C_3H_6, 12o/o of C_3H_8) from the content of the inert components as which they are used carbon dioxide and water of pairs. These data to a certain degree characterize also the effect of pressure on the limits of explodabilities, which were determined for mixtures with CO_2 with 1 and 7 at. Experiments on the mixtures, which contain carbon dioxide, are carried out at room temperature, experiments on water vapor - at 100°C. Of binary mixture (C_3H_8) + O_2 with 1 at α_{min} virtually coincides with the value, which corresponds to the recommended [135] upper concentration apparitor for pure/clean propylene.

The value α_{min} is little affected over a wide range of a change of the concentration of inert component, in particular with 1 at.

Table 14. Limits of explosiveness of the -mixtures of technical hydrocarbons with oxygen.

(1) Горючее	(2) Содержа- ние, %	$[O_2]_{кр}$ %	α_{min}	(1) Горючее	(2) Содержа- ние, %	$[O_2]_{кр}$ %	α_{min}
(C_3H_8)	100	49,0	0,220	(C_4H_{10})	30		
(C_4H_{10})	100	52,0	0,171	(C_3H_8)	15	63,0	0,604
(C_3H_8)	100	46,5	0,196	CO	50		
(C_4H_{10})	75	46,5	0,145	N_2	5		
(C_3H_8)	25			(C_3H_8)	60		
(C_4H_{10})	80			(C_3H_8)	17	50,7	0,221
CO	15	60,8	0,301	CO	20		
N_2	5			N_2	3		
(C_4H_{10})	60			(C_3H_8)	30		
(C_3H_8)	18	55,7	0,267	(C_3H_8)	15	62,4	0,746
CO	20			CO	50		
N_2	2			N_2	5		

Key: (1) Fuel; (2) Content.

Table 14. Limits of explosiveness of the mixtures of technical hydrocarbons with oxygen.

Key: (1). Fuel. (2).

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With an increase of the content of carbon dioxide, critical oxygen concentration monotonically is lowered from 46o/o in binary mixture (I = 0) to 15o/o of "cape" (Y for 1 at. Thus, in the mixtures, fuel-rich, the additions of inert component do not exert themselves the flegmatizing action/effect, but on the contrary, they increase explosiveness, if it are are measured by saturated oxygen concentration.

With a pressure increase, the region of dangerously explosive compositions somewhat is expanded. For binary mixtures in the range between 1 and 7 at value α_{min} is changed approximately in time, this corresponds $-d \lg \alpha_{min} / d \lg p = \varepsilon = 0{,}36$. For the mixtures, which contain 50o/o of CO_2, effects of a change in the pressure weakens to $\varepsilon = 0{,}18$. The replacement of carbon dioxide by water vapor a little

expands the limits of explodability. relation α_{min} $(CO_2)/\alpha_{min}$ (H_2O) reaches maximum value of 1.6 with I = 60o/o.

Presented facts confirm the impossibility of the utilization of additions of inert gases the target/purposes of the intensification of technological process for the rich mixtures containing oxygen: these additions are here ineffective. At the same time in the processes of the gas-phase oxidation of hydrocarbons, is possible the utilization of carbon monoxide as that flegmatizing additions. Among the systems, which are encountered in the chemical technology, the effect of inhibition is most sharply pronounced during the oxidation of the rich mixtures of hydrocarbons and carbon monoxide. A conversion of hydrocarbons it is expedient to realize under the conditions of the recirculation of the mixtures, inhibited by additions CO.

In this process it will be possible to noticeably increase oxygen content. The utilization of carbon monoxide favors the fact that it forms in the very oxidation process of hydrocarbons; with convection it is not expend/consumed. The end products, capable easily to be condensed, one should derive/conclude from the sphere of

reaction into which is added hydrocarbon-oxygen mixture with its consumption. It is possible to expect that the additions of carbon monoxide will contribute not only to safeguard explosion safety, but also to the course of the process of conversion in desirable direction, braking the side reactions of a deep oxidation of oxide products.
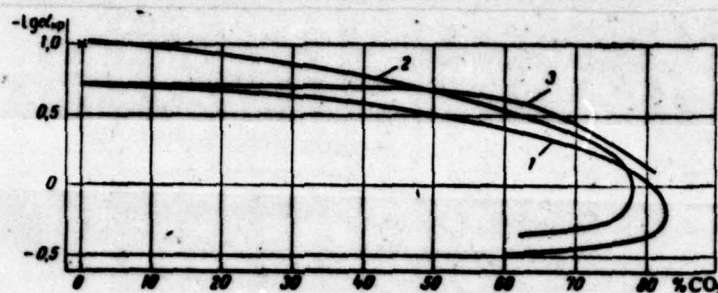
Fig. 57. Critical values of excess oxidant ratio for mixtures of technical propylene with oxygen: 1 - mixture with CO_2, 1 at; 2 - the same, 7 at; 3 - mixture with H_2O, 1 at; x - limit of explodability of mixtures of pure/clean propylene, 1 at [135].

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In the processes of oxidative conversion, one should especially strictly track the fact so that would not be formed the explosive mixtures, since they can be not only set fire by the discharges of static electricity, but also they can ignite spontaneously in the reactor of oxidation. For such systems were recorded very low values of the temperature of self-ignition p to close to operating temperature of conversion.

Steam-oxygen conversion of methane in mine/shaft reactors [210]. The bulk of hydrogen for the synthesis of ammonia is produced at present by the method of the mine/shaft steam-oxygen conversion of hydrocarbons. The converted mixture of combustible gas, oxygen and water vapor passes through the catalytic gas recombiner with packing from the grains of nickel catalyst. Apparatus by diameter 1.5-3 m, by the productivity of order of tens of thousands of nm^3/h, is equipped with fireproof lining. As basic raw material for many Soviet plants serves natural gas with the content from 82 to 98o/o of methane.

The process of conversion is conducted according to low-pressure patterns (1.5-3 at) or of mean pressure (by 20-30 at). For conversion are used either of technical oxygen, which contains 82-98o/o of O_2 or concentrated by atmospheric oxygen (40-50o/o of O_2). In the steam-oxygen process of mean pressure, the oxygen content in treated mixture is approximately 15o/o, water vapor - about 62o/o. For low-pressure, process is characteristic the oxygen content 26o/o, of water vapor - 37o/o. In the case of steam-oxygen-air conversion at the pressure, close to atmospheric, the reaction mixture contains about 20o/o O_2 and 50o/o (H_2O + N_2). The temperature of preheating in all cases is close to 400-500°C.

cases is close to 400-500°C.

During the normal flow of technological process, methane reacts with oxygen and water vapor without the emergence of flame and soot formation. However, this conditions/mode not always is retained: under certain conditions above the catalyst bed, appears stationary flame, which is led to a sharp increase in the temperature. The result of this complication proves to be the burning out of metal insert/reinforcement, the destruction of the grains of catalyst and lining of converter. To the destruction of refractories, is led not so much the reheat, as sharp thermal shock; catalyst is crushed in the process of gasification by water vapor of the plotted on it soot.

In connection with these complications it is necessary to determine the boundaries of explodability in system CH_4 + O_2 + H_2O with appropriate pressures and the contents of inert component. In view of the absence of these direct measurements, this problem is solved by the method of modelling. For basis it is possible to accept the presented in Fig. 57 results of the measurement of the limits of explodability for system (C_3H_8) + O_2 + H_2O. Problem consists in the check of the degree of the similarity of

both systems and in the estimation of error in simulation, and also in the determination of the baric coefficient of the limits of explodability.

End Section.

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Indicated the curves of dependences $\alpha_{xp}(l)$ with 1 at in Fig. 58 are compared with data other investigations. Values α_{min} for the binary mixtures of a series of combustible substances with oxygen [135] satisfactorily will agree between themselves, and also with analogous value for model fuel - technical propylene. This makes it possible to consider that for I > 0, i.e., for the unstudied three-component mixtures of the same fuels, value α_{xp} are sufficiently close to analogous value of the mixtures of model fuel. The great deviation of value α_{min} of binary mixture from the appropriate value for model fuel is observed for methane. Apparently, this is bonded not with the error of experiment, but with the known specific character of the rich mixtures of methane.

In several old works is investigated the behavior of carbon dioxide as that flegmatizing additions to the mixtures of the carbon-containing fuels with oxygen. Their converted results are also represented in Fig. 58. These

[211] and [212] for mixtures $CH_4 + O_2 + CO_2$ give the knowingly lowered contents of fuel on upper limit in connection with the insufficient width of combustion tube and the ignition of the mixtures being investigated of its upper end. For $I = 0$ value $(-lg\alpha_{min})$ in these works than somewhat less recommended [135] for methane. At the same time the curve of the dependence $lg\alpha_{min}$ from I is arrange/located approximately by the equidistantly appropriate curve for model fuel. Experiments [213] were conducted with mixtures $(CH_3)_2 CO + \overset{O_2+}{\wedge} CO_2$ and $CH_3OH + O_2 + CO_2$ with the high content of inert component, these data make it possible to check the position of the cape of the region of explodability. The obtained results satisfactorily will agree with data for model fuel.

The presented facts make it possible to consider establish/installed that system $(C_3H_6) + O_2 + CO_2$ can serve model for system $CH_4 + O_2 + CO_2$. Hence follows the second conclusion: system $(C_3H_6) + O_2 + H_2O$ is model for system $CH_4 + O_2 + H_2O$; recall that with identical fuels α_{min} for mixtures with both inert components they differ not more than 1.6 times. Standardized values of the limits of the explodability of model system can be with known "safety margin" disseminated to the appropriate compositions of the

unstudied system at whose value $(-\lg \alpha_{min})$ is somewhat less. Judging by the positions of limits with $I = 0$, actual critical oxygen content in mixtures with methane must be by approximately 30o/o more than calculated.
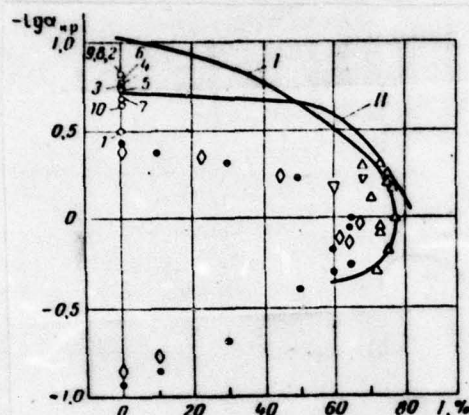
Fig. 58. Limits of explodability in system fuel + of O₂ +
I with 1 at. Model mixtures (C₃H₆): I - I = CO₂; II -
I = H₂O, mixture with [I] = 0: 1 - CH₄; 2 - C₂H₆; 3 -
C₃H₈; 4 - n - C₄H₁₀; 5 - from - C₄H₁₀; 6 - C₆H₁₄; 7 -
propylene; 8 - C₆H₆; 9 - cyclohexane; 10 - (CH₃)₂O. Fuel
+ of O₂ + CO₂: Δ - is acetone [213]; ∇ - is methanol
[213]; ◊ - are CH₄ [211]; • - are CH₄ [212].

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On the effect of pressure on the limits of the
explodability of mixtures CH₄ + O₂ + H₂O, it is possible

to judge on the basis of the information, given in the preceding section, and also direct measurements for binary mixtures $CH_4 + O_2$ [214]. The converted results [214] are represented in Fig. 59, which gives $\varepsilon = 0.35$. This condition can be disseminated also to three-component mixtures $CH_4 + O_2 + H_2O$. This assumption is also bonded with certain increase in the "safety margin". Judging by the behavior of other combustible systems, value decreases with an increase of the content of inert components.

Accepting, that the limits of explodability in system $CH_4 + O_2 + H_2O$ correspond to curve II of Fig. 58 and to condition $\varepsilon = 0.35$, it is possible to calculate values of saturated compositions. Figures 60 and 61 gives to the dependence of saturated oxygen concentrations (minimum) or respectively of methane (maximum) on the concentration of water vapor. Each of the curves is related to pressure 1, 5, 10, 20 and 40 at respectively even 100°C. Since the accepted by us value of the baric coefficient of the limits of explodability ε, apparently, somewhat higher than curves which determine critical oxygen concentrations with r > 1 at (Fig. 60), are must, in actuality, to be found somewhat it is nearer to curve for 1 at.

If we consider the difference α_{min} of the mixtures of methane and model mixtures, calculated saturated oxygen concentrations are somewhat understated, but methane concentrations are overstated. However, it is necessary to consider that the temperature of the converted mixtures on 300-400 degrees higher than in experiments on model mixtures. It is possible to assume that the effect of an increase in the temperature compensates for the effect, caused by chemical specific character, and the obtained critical concentrations approximately correspond actual.

As during the conversion of propylene, critical oxygen concentration decreases with an increase in the content of water vapor. Only at very high [H_2O] is reached gently sloping minimum.
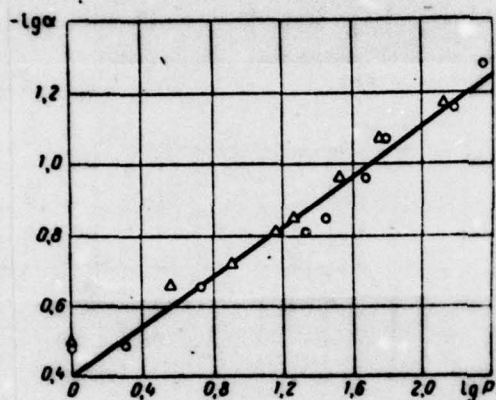
Fig. 59. Effect of pressure on limits of explodability according to data [214]:   o – burns;   Δ – does not burn.

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In In the process of the conversion of methane with 20 at in connection with the high content of water vapor – 60o/o – the limiting concentration taking into account three-component mixture is small: about 6o/o. Since in this case are processed the mixtures, which contain 2.5 times of more oxygen, they are unconditionally combustible. The same it is possible to say, also, about the mixtures, processed

during the steam-oxygen low-pressure process and
steam-oxygen-air process. Within the limits of technological
conditions/mode composition cannot be changed so in order to
make the processed mixtures nonexplosive.

Since it is not possible to create the condition of
the normal course of process within the framework of the
observance of the first principle of safety, the formation
of the centers of combustion it is necessary to prevent by
means which correspond to the second principle. The
processed mixtures, although are explosive, all the same are
related to slowly burning and therefore difficultly ignited.
The conversion of methane is conducted in rapid flow, which
impedes the emergence of stationary flame. Smooth burning
will prove to be impossible, if we within converter remove
stagnation zones and the large free space, filled by
combustible mixture.

The stagnation zones, in which the rate of gas flow
descends virtually to zero, can occur in spite of the
significant average discharge velocity of the converted
mixture (5-80 m/s). Combustion in such zones is the reason
for the destruction of the mixing devices of many
installations, working. For this reason the speed of ordered

flow of gas along apparatus can be lowered only after a decrease in oxygen concentration down to the value smaller than saturated.
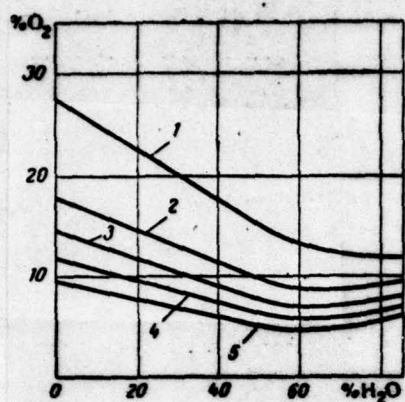
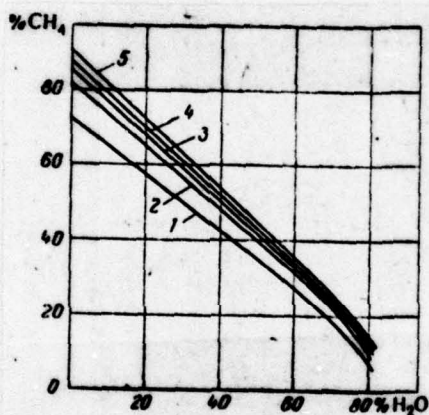Fig. 60. Saturated oxygen concentrations in system $CH_4 + O_2 + H_2O$: 1 - 1 at; 2 - 5 at; 3 - 10 at; 4 - 20 at; 5 - 40 at.

Fig. 61. Limiting concentrations of methane in system $CH_4 + O_2 + H_2O$: 1 - 1 at; 2 - 5 at; 3 - 10 at; 4 - 20 at; 5 - 40 at.

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Another reason for the emergence of flame in converters

consists in the local deviation of the composition of gaseous mixture from average value, caused by the poor mixing of components. Any fluctuations of composition are bonded with formation in the specific sections more explosive and easily ignited mixtures. Practice shows that the emergence of the centers of combustion is usually caused by jumps in pressure of components in grid/network and of their consumption. This is led to the deviation of composition from that which was assigned, at least local and short-time. Since the mixture of normal composition is also combustible, the formed flame proves to be resistant, also, after returning of the conditions/mode of process to that which was assigned.

As a result of the emergence of the center of combustion, is disturbed the temperature conditions of converter, in particular grow/increases the inlet temperature into contact zone and in frontal catalyst bed. Simultaneously sharply grow/increases the effective hydraulic friction of contact zone, also, in frontal catalyst bed. Simultaneously sharply grow/increases the effective hydraulic friction of catalytic gas recombiner, i.e., pressure difference at entrance and exit as a result of the expansion of gas with combustion. According to these indices

it is possible to judge the emergence of flame. It is
obvious that with ignition in converter a decrease in the
consumption of mixture is not led to end of burning, but
makes flame only more stable. To extinguish the flame is
possible only by appropriate change in the composition.

The most effective methods of preventing the formation
of the centers of combustion during the conversion of
methane consist in the intensive mixing of blending agents
with the target/purpose of the achievement of its
homogeneity and in the exception/elimination of the
possibility of the origination of stagnation zones. These
zones in many instances can be removed by means of blowout
by water vapor of the upper sections of mine/shaft
converters.

Effective mixing can be reached during the utilization
of mixing device which is bundle from the ducts, staggered,
installed within the basic wide duct of mixer, which leads
in reactor, in planes normal of its axis. In the lateral
surfaces of tubes at equal distances, are made the
opening/apertures, through which the gas, supplied into
tubes, enters basic duct. To basic duct is supplied the
mixture of water vapor with fuel, through the

opening/apertures of the bundle of tubes - the missing
blending agent, i.e., oxygen (or the mixture of air with
oxygen) if necessary diluted by a minimum quantity of water
vapor. In this oxygen supply system, appear many small
parallel streams of the mixed gases; mixing length normal
to the direction of flow, proves to be small. On the
other hand, the bundle of tubes, placed across flow,
produces its strong agitation facilitating mixing.

Low-temperature oxidation of ethylene [215]. The
catalytic oxidation of ethylene by oxygen to acetaldehyde
presents by itself important and extremely promising
technological process. This method consists in the bubbling
of the mixture of ethylene with oxygen through the aqueous
solutions of salts of platinum metals, in particular
palladium, with the additions of copper salts or gland
[216, 217]. Under appropriate conditions the dissolved salt
retains stability, playing the role of catalyst.

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The effective conducting of oxidation is strongly
complicated by the explosiveness of ethylene-oxygen mixtures
over a wide range of compositions - from 3.0 to 80o/o C_2H_4

in binary mixtures at one at. For such mixtures α_{min} = 0.083, i.e., it is substantially less than for paraffins and propylene (0.15-0.20). This special feature/peculiarity of the mixtures of ethylene is caused by its high endothermicity; therefore excess ethylene proves to be so weak a stabilizer.

Technological process is conducted at the pressures, more than atmospheric, for which it is possible to expect the further expansion of the limits of explodability. At the same time for the intensification of technological operations, is desirable a maximum increase of oxygen concentration in the converted rich ethylene-oxygen mixtures. The urgency of this problem is caused not only by the smallness of saturated blasting oxygen concentration, but also by its weak solubility in water, i.e., in the sphere of main reaction, 4 times less than in ethylene. During the estimation of the possibilities of intensification, it is necessary to consider not only the effect of pressure on the limits of explodability, but also presence in the processed mixtures of inert component - water vapor.

During the study of the limits of explodability in system C_2H_4 + O_2 + I and the effect on them of pressure

was used as during the investigation of the mixtures of propylene, the method of model inert component. In view of the difficulty of experimentation with water by vapor, it they replace by carbon dioxide. The results of these investigations are represented in Fig. 62 in the form of the dependence of the critical pressure by which still possibly the ignition of mixture, from the content in it of oxygen.

At 20°C pressure increase from 1 to 18 at decreases the critical oxygen content $[O_2]_{\kappa p}$ in binary mixtures 2.3 times, at 130°C pressure increase from 1 to 10 at is led to decrease $[O_2]_{\kappa p}$ 2.2 times. For the mixtures, which contain 40o/o of CO_2, pressure increases from 1 to 18 at is changed $[O_2]_{\kappa p}$ at 20°C 1.9 times. The comparison of all obtained results shows that an increase in the temperature on 110°C decreases the critical oxygen content $[O_2]_{\kappa p}$ from 10 to 20o/o of its value, i.e., on ~2o/o O_2 of absolute. This will agree with data [144], and also [178].

At the fixed/recorded pressure the addition 40o/o CO_2 increases saturated oxygen concentration taking into account binary mixture within the limits of two times. However, if we relate oxygen content to the entire three-component

mixture C_2H_4 + O_2 + CO_2, then value $[O_2]_{kp}$ at p = const, does not in practice depend on the content of inert component.

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are given below the absolute values of saturated oxygen concentration in mixtures C_2H_4 + O_2 + CO_2:

% CO_2	Давление, ат (1)		
	5	10	15
0	15,7	11,8	10,3
10	16,0	13,6	12,1
40	14,5	12,5	12,1

Key: (1). Pressure, by at.

Compare regularities for the limits of the explodability of similar mixtures C_2H_4 + O_2 + CO_2 and (C_3H_6) + O_2 + CO_2.

The replacement of excess fuel by inert component makes more dangerously explosive the rich mixtures of propylene: with an increase in concentration CO_2 from zero to 40o/o, saturated concentration of oxygen is lowered from 46 to 32o/o. As a result of the nonsaturation of ethylene, the

absolute value of the limiting concentration of the missing component in the rich mixtures C_2H_4 does not descend with an increase in the content of inert diluent.

Greater in comparison with other fuels the reserve of energy of the analogous mixtures of ethylene complicates the problem of the desensitization of these mixtures and the safeguard for explosion-proof character of their conversion. Under sufficiently rigorous conditions - at temperature of 330-360°C and the pressure of 50-175 at the decomposition of ethylene in the heated vessel can lead to spontaneous ignition [218, 219]. Since with an increase of pressure decreases saturated oxygen concentration, by which still possibly flame propagation in mixtures $C_2H_4 + O_2$ under certain conditions, apparently, is attained also blasting the decomposition of cold ethylene, such as in acetylene and nitrous oxide.

In spite of the special feature/peculiarity of the rich mixtures of ethylene with oxygen, the baric coefficient of the limits of explodability has approximately the same values, as for other combustible systems. Figures 63 depicts the critical parameters in the form of dependence $\lg \dot{\alpha}_{min} - \lg p$, which for all $[CO_2]$ and T_0 it is possible to approximately

consider linear. For binary mixtures value $\varepsilon = (-d \lg z_{min} / d \lg p)$
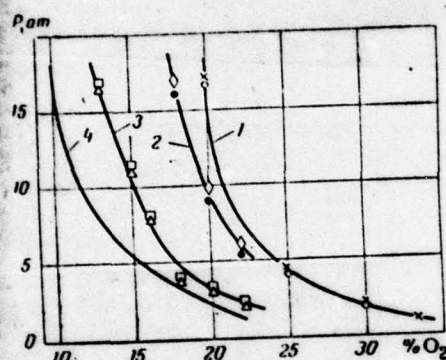= 0.36, at concentration CO_2 40o/o it decreases to 0.24.

Fig. 62. Dependence of critical pressure of explodability in
system $C_2H_4 + O_2 + CO_2$ on oxygen content: 1 - 40o/o of
CO_2, 20°C; 2 - 40o/o of CO_2 130°; 3 - 10o/o of CO_2 20°;
4 - 0o/o CO_2;   20°; x, ◇, □ - it burns;   ⊙, ●, △ - does
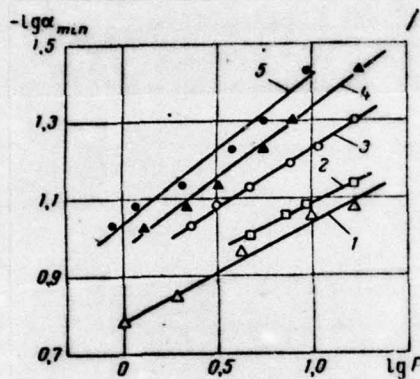not burn.

$[am = at]$

Fig. 63. Effect of pressure on limits of explodability in system $C_2H_4 + O_2 + CO_2$: curved 1 - 4 see Fig. 62; 5 - 0o/o of CO_2, 130°.

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Thus, the established/installed for a series of other combustible mixtures character of the dependence of the upper limit of explodability from pressure, apparently, can be considered universal and with satisfactory accuracy disseminated to the unstudied gas systems. For the rich mixtures of fuel with oxygen and inert component it is

proportional to root from the third to fifth degree from the value of pressure. Exponent decreases with an increase in the content of inert component. The lower limit of explodability, which proved to be for a binary mixture equal to 2.85o/o of C_2H_4, does not in practice depend on pressure, as this was observed for other combustible mixtures.

The special properties of ethylene-oxygen mixtures will force to be restricted to following recommendations for the conversion of the mixtures, containing of inert component from 0 to 40o/o. With the necessary 30-40o/o "safety margin" maximum permissible oxygen concentrations taking into account binary (in this case - dry) mixture are 9-14o/o for 5 at even 6.5 - 12o/o for 10 at. Such low values of limiting concentrations substantially affect the intensity of technological process.

For increasing the possibilities of a safe increase in oxygen concentration in the processed mixture it is expedient to use addition method mentioned above (see Chapter 7, pt. 1) of alien combustible component. As such that flegmatizing additions, it is possible to use saturated hydrocarbons. at the low temperature of process - order

100-190°C - these hydrocarbons will play the role of knowingly inert components and at the same time they will considerably increase saturated oxygen concentration. It is possible to introduce them into the reaction cycle where they will not take part in reaction; the content of ethylene and oxygen in mixture is supplemented with their consumption.

The evaluation of the effectiveness of this method can be made according to the method of model component. For this, we will use the available data on the limits of the explodability with of 1 at rich mixtures in ethylene - cyclopropane - oxygen ternary system [135]. These data it is expedient to present in the form of the dependence α_{min} on the portion of ethylene in the sum of combustible components taking into account from the stoichiometric coefficients

$$\beta = \frac{3 [C_2H_4]}{3 [C_2H_4] + 4.5 [C_3H_6]}$$ (7.3)

Are given below standardized values of the limit of explodability in system C_2H_4 - C_3H_6 - O_2:

β	0	0.181	0.306	0.485	0.653	0.801	1.00
α_{min}	0.148	0.158	0.147	0.121	0.106	0.0898	0.0838

The limit of explodability for cyclopropane (β = 0) in

standardized system does not differ from the common for paraffin hydrocarbons (see above). As a result of the larger activity of ethylene, value α_{min} in ternary mixtures is less than for the binary mixture of cyclopropane. However, this effect is noticeable only when when $\beta >$ 0.3-0.4, when smaller β the limit of the same as for the saturated hydrocarbons.

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The identity of limits for the binary mixtures of cyclopropane and for the mixtures of paraffin hydrocarbons makes it possible to assume that standardized values of the limits of the ternary mixtures of paraffins with ethylene and oxygen will be approximately by the same as in the equivalent mixtures $C_3H_6 + C_2H_4 + O_2$. This makes it possible to calculate maximally allow small oxygen content in the technological mixtures, flegmatized by the additions of saturated hydrocarbons.

With the low contents flegmatizing additions its effect will be too weak, with large - a noticeable decrease in ethylene concentration will begin to affect the reaction rate. It seems it is expedient to convert mixtures with

the equimolecular content of stabilizer and ethylene. The flegmatizing effect of addition and the corresponding change in maximum permissible oxygen concentration depend on the stoichiometric coefficient of the reaction of the complete combustion of this product and, consequently, also its molecular weight.

during the equimolecular dilution of ethylene by ethane critical oxygen concentration for 1 at in dry gas grow/increases to 28.4o/o, i.e., by 41o/o of original value. More effective proves to be butane, which increases under analogous conditions saturated oxygen concentration to 41.2o/o, or 2.1 times. The application/use of hydrocarbons with great molecular weight is inexpedient in view of the insufficient pressure of their saturated steam at room temperature. For obtaining the mixtures of the corresponding composition, will be required the thermostating of entire equipment in technological cycle.

As it was shown above, the baric coefficients of the standardized limits of explodability barely depend on the nature of fuel. This makes it possible with good accuracy to calculate the maximum permissible oxygen contents at a pressure of more atmospheric, and also during dilution by

the inert blending agent of fuel and oxygen. Are given below oxygen concentrations in dry mixture with equimolecular contents ethylene and butane (taking into account the same "safety margin") depending on pressure (in at) and the content of inert component (in o/o):

(1) Давление	Содержание инертного компонента (2)		
	0	10	40
5	19,5	21,5	28,5
10	17,0	19,0	25,5

Key: (1) - pressure. (2) - Content of inert component.

The converted vapor-gas mixture, saturated at by 130°C water vapor, contains at the total pressure of 5 at 55o/o H$_2$O and with p = 10 at 27o/o H$_2$O. Hence it follows that under the condition of saturating the components by water vapor before their mixing it is possible to process the mixtures, which contain 30o/o of O$_2$ with p = 5 at and 24o/o of O$_2$ with p = 10 at.

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Thus, the conversion of the equimolecular mixture of ethylene and butane makes it possible to safely increase more than double the oxygen content in the processed mixtures.

It is easy to ascertain that the optimal relationship/ratio of the contents of ethylene and butane in

the converted mixture approximately coincides with equimolecular. So, with p = of 7 at even 130°C in the case of m = $[C_2H_4]$: $[C_4H_{10}]$ = 1: 3 oxygen content can be increased 1.11 times in comparison with the system in which m = 1: 1. In this case,, however, the content of ethylene too strongly is lowered: from 36.5 to 17.8o/o taking into account dry mixture; the high partial pressure of butane in of systems it will require the preheating of all assemblies of unit to 40-50°C. Under the same conditions with m = 3: 1 is admissible an increase in the oxygen content in comparison with the concentration, which corresponds to m = -. only to 20o/o.

The flegmatizing action/effect the addition of butane checked experimentally. In set of experiments during which the equimolecular mixture of butane and ethylene mixes with oxygen and carbon dioxide with such calculation, which the content of the latter always comprises gender with such calculation, that the content of the latter always was 40o/o, saturated oxygen concentration with 7 at even 130°C was equal to 25.5o/o. Taking into account equimolecular mixture without inert component, saturated concentration of oxygen is equal to 42.6o/o. As can be seen from Fig. 62, under analogous conditions for a mixture with pure ethylene

(n = -) saturated oxygen concentration is equal to 21o/o. Thus, experimental check confirms the designed double increase in saturated oxygen concentration during the replacement in the conversion gas of ethylene by its equimolecular mixture with butane.

Specific additions. In those cases when one of the components of complex mixture catalyzes or inhibits the oxidation process (for several oxidizers - process of reduction) of another component, is observed the specific deviation of the standardized value of the limit of explodability from the normal for similar systems. This deviation the greater, the stronger the effect additions on reaction kinetics in flame at the fixed value of combustion temperature. The specific effect of chemical active addition, or on the contrary, its absence when this action/effect for any reason was expected that they have vital importance for the problems of explosion-proof character technique.

during the study of the processes of burning and ignition of complex gaseous mixtures, obtained many examples of the inhibition of the oxidation by oxygen of one of fuels tby another, but sometimes also mutual inhibition. So, in a series [220-224] is establish/installed the inhibition

of the oxidation of hydrogen by additives of hydrocarbons in the mixtures, fuel-rich. With respect to hydrocarbons excess hydrogen behaves as inert component.

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Kurtz [225] established the inhibiting effect the addition of sulfurous and selenide hydrogen on the oxidation of hydrocarbons and the inverse effect, which increase with an increase in the relation of the contents of fuel and oxidizer. This effect is specific for these substances, other hydrides [1], for example ammonia, do not exert this effect.

FOOTNOTE [1]. In author's concept, hydrides, supplying atomic hydrogen, they must accelerate the oxidation reaction. ENDFOOTNOTE.

The specific inhibition of oxidation is reveal/detected by Kurtz also for the mixtures of propane and diborane [226]. meIn these works with the change f the relationship/ratio of the contents of fuel and oxidizer from $\alpha > 1$ to $\alpha <$

1 is observed the transition from catalysis to inhibition. To greater degree this is characteristic for the oxidation of the mixtures of hydrocarbons and carbon monoxide. Of rich mixtures is observed the mutual inhibition of oxidation, of lean and close to stoichiometric - the acceleration of oxidation, which leads to an increase in velocity and stability of flame [227-229].

The phenomenon of inhibition, essential for the problems of explosion-proof character technique, is observed also of other systems. As inhibitors can serve the additions of more active combustible or oxidizer. So, the pairs of the mentioned ethyl mixture P-9 contain, besides basic component - ethyl bromide, the small additions of ethyl chloride and gasoline. Both these products are more active fuel, than ethyl bromide, have the wider limits of explodability. However, as can be seen from Fig. 64, in multicomponent mixtures the limits of explodability become narrow - both more active components inhibit the oxidation ethyl bromide [206]. As it was noted above (chapter 7, pt. 1), the presence of inhibitor affects the value only of upper limit of explodability.
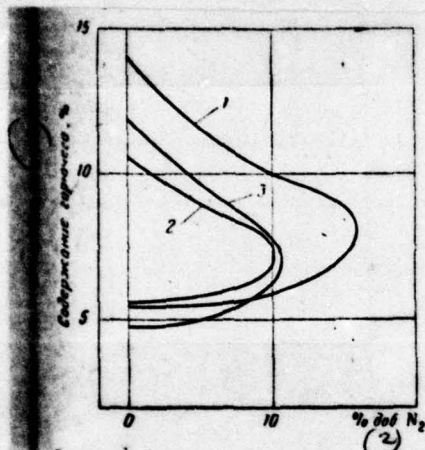
Fig. 64. Effect addition on limits of explodability of mixtures ethyl bromide with air hand nitrogen; composition of fuel: 1 - 100o/o C_2H_5Br; 2 - 90o/o C_2H_5Br + 10o/o C_2H_5Cl; 3 - 95o/o C_2H_5Br + 5o/o of gasoline.
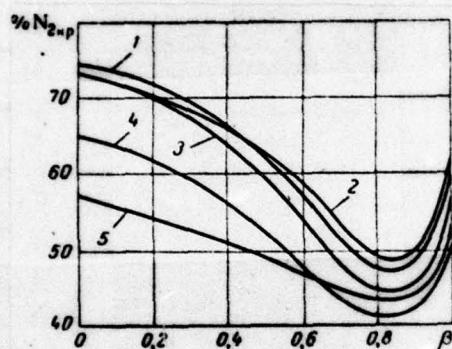
Key: (1). Content of combustible, %о; (2). Pressure.

Fig. 65. Dependence of limiting concentration of flegmatizing nitrogen in mixtures $C_6H_{12} + NO + N_2O + N_2$ on composition of oxidizer: 1 - lg α = 0; 2 - lgα = -0.1; 3 - lgα = 0.1; 4 - lgα = 0.2; 5 - lgα = -0.35.

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The mutual braking of reaction in flame is observed also for the mixtures of oxide and nitrous oxide with hydrocarbons [230]. Nitrous oxide - much more active

oxidizer, than oxide, its analogous mixtures are explosive within wider limits, than the mixture of nitrogen oxide. However, the region of combustible compositions for the mixtures, which contain both oxidizers, it is narrower than for analogous mixtures with each of them.

This illustrates Fig. 65, in which is shown the dependence of saturated concentrations of flegmatizing nitrogen b fuel-rich mixtures C_6H_{12} + NO + N_2O + N_2 on the portion of nitrogen oxide in the sum of the contents β = [NO] /([NO] + [N_2O]) for a series of the fixed values of the excess oxidant ratio. The mixtures, which correspond to the minima of curves $l_{кр}(\beta)$, are combustible in the narrower range of compositions, than analogous mixtures with each of the individual oxidizers - N_2O or NO. The great narrowing of the region of dangerously explosive compositions corresponds β = 0.80-0.85. In the mixtures of which the oxidizer consists to 40-50o/o of N_2O, the limits of explodability the same as for the analogous mixtures, which contain only oxide of nitrogen.

The characteristic example of system with specific additions are combustible mixtures, containing minor constituents of carbon disulfide. It is known that carbon

disulfide is one of most complex and the unpleasant from
the viewpoint of the explosiveness of the objects of the
chemical technology. As is evident the view of the
explosiveness of the objects of the chemical technology. As
can be seen from survey/coverage of the dangerously
explosive properties of carbon disulfide and recommendations
regarding work with it [231, 232], the complexity of
inversion with it containing oxygen by mixtures is caused
by the extremely broad band of dangerously explosive
compositions and ease of the emergence in them of flame
during the smallest heating. Therefore the safety regulations
introduce very severe limitations on the regulations of work
in the rooms, dangerous in the relation to the possibility
of presence in their atmosphere the pair of carbon
disulfide.

The limits of the explodability of carbon disulfide in
mixture with air are considered equal to 1.25-50o/o that
corresponds $\alpha_{кр}$ = 5.6-0.070, i.e., to the considerably more
broad band of compositions, than for the air mixtures of
other fuels. However, under certain conditions the mixtures,
which contain the hundredth and even thousanths of
percentage CS_2, prove to be fuels. The mixtures of carbon
disulfide ignite spontaneously in the heated vessel narrower
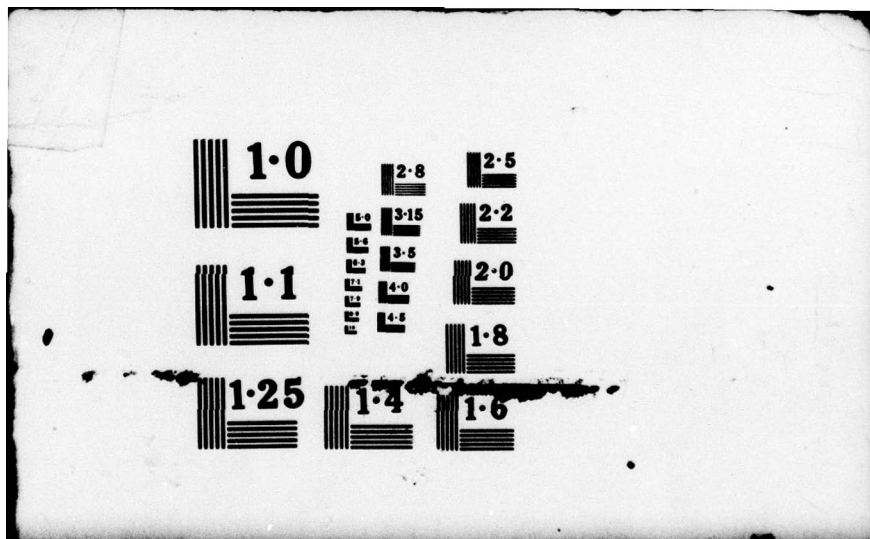
at 100-120°C, and sometimes even at 80°C [233, 234]. Is especially dangerous the capability of these mixtures for the low-temperature ignition of the outside closed vessel (see Chapter 9).
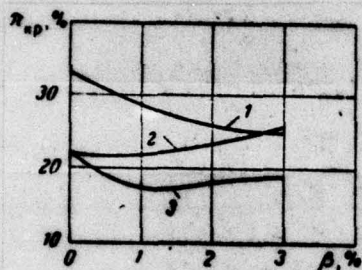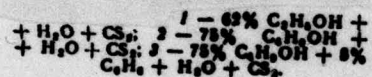
Fig. 66. ~~Effect~~ addition of carbon disulfide on limits of explodability of rich air mixtures; composition of fuel: $1 - 69\%$ C_2H_5OH $+ H_2O + CS_2$; $2 - 75\%$ C_2H_5OH $+ H_2O + CS_2$; $3 - 75\%$ $C_2H_5OH + 8\%$ $C_6H_6 + H_2O + CS_2$.

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These properties of the mixtures of carbon disulfide are caused by its tendency toward the formation of cold flames. However, the possibility of the emergence of cold flame is not equivalent the possibility of its transition also to hot flame. Between only this transition in the final analysis is essential for explosion-proof character technique.

In set of experiments [235] is studied the

action/effect the addition of carbon disulfide on the limits of the explodability of the fuel-rich air mixtures of ethyl and butyl alcohols. Content CS_2 in the mixture of fuel and water composes to 3 mol. o/o. As can be seen from the curve/graph of Fig. 66, value α_{nn} with practically constant $I = 64-68\%$ is only insignificant, and besides unspecific, is changed with the increase in the content of carbon disulfide. the impurity/admixtures of carbon disulfide in fuel-rich mixtures, in spite of $I = 64-68\%$ expectations, do not have any characteristic effect on the limits of explodability. In the case of air suction into apparatuses with fuel, the explosiveness does not depend on possible presence the addition of carbon disulfide and is defined by the standardized limits of explodability, in principle by the same as other combustible systems.

The additions of carbon disulfide do not affect also the ignition temperature during heating by adiabatic compression. For an oxyhydrogen mixture value T_c

is not virtually changed with addition 2o/o CS_2. value T_c of mixture $CS_2 + 4O_2$ only to 150-200 degrees is lower than in mixture $2H_2 + O_2$ [94]. The low-temperature autoacceleration of reaction is specific for the conditions under which is possible the development

of cold-flame process. During ignition by the electric discharge of fuel-rich mixtures with additions CS$_2$ and during adiabatic ignition chain process with the degenerate branchings does not manage to arise.

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